TABLE I

SUMMARY OF ANALYTICAL RESULTS

	C	N	Cu	Combustion Water	Atom D
Calcd. for $(C_8H_4N_2)_4H_2$	74.69	21.78		31.51	0.016
Found	74.74	21.82		31.44	0.016
Calcd. for $(C_8H_4N_2)_3$ Cu	67.18	19.45	11.03	25.02	0.016
Found	67.23	19.51	11.02	24.96	0.016
Found for $(C_8H_4N_2)_4$ Cu treated with D_2SO_4 and D_2O	67.20	19.48	11.01	25.00	0.065
Calcd. for $(C_8H_4N_2)_4$ D_2	74.40	21.69		31.78	11.11
$(C_8H_4N_2)_4D_2$ obtained from $(C_8H_4N_2)_4H_2$					
5th crystallization	74.40	21.70		31.74	11.10
6th crystallization	74.43	21.66		31.79	11.12
$(C_8H_4N_2)_4D_2$ obtained from $(C_8H_4N_2)Li_2$					
5th crystallization	74.42	21.63		31.80	11.10
6th crystallization	74.44	21.68		31.77	11.09

pyrrole NH bonds.[3] Since a band at this frequency has also been observed for copper phthalocyanine,[4] it would appear unlikely that it is assignable to NH. If such an NH bond were present one would expect to find an ND bond peak at 2333 cm.$^{-1}$ in deuterio-phthalocyanine with concomitant disappearance of the 3298 cm.$^{-1}$ peak. We observed a weak band at 3298 cm.$^{-1}$ in phthalocyanine, deuterio-phthalocyanine, and copper phthalocyanine but failed to observe any peaks in the region 1700 to 3200 cm.$^{-1}$ in the spectra of the deuterio-phthalocyanine, its spectra being identical to that of phthalocyanine over the range 850 to 4000 cm.$^{-1}$

EXPERIMENTAL

Dilithium phthalocyanine was prepared according to Barrett,[5] and recrystallized from anhydrous acetone–benzene to constant analysis.

Phthalocyanine was prepared from dilithium phthalocyanine by solution in 100% sulfuric acid followed by dilution with water,[5] at 0°, and recrystallized from sulfuric acid–water to constant analysis.

Copper phthalocyanine was prepared from dilithium phthalocyanine and anhydrous cupric chloride[5] and recrystallized from sulfuric acid–water, at 0°, to constant analysis.

Deuterio-phthalocyanine (method 1) was prepared from dilithium phthalocyanine by solution in 100% deutero sulfuric acid followed by dilution with deuterium oxide at 0° and recrystallized from deuterosulfuric acid–deuterium oxide to constant analysis.

Deuterio-phthalocyanine (method 2) was prepared from phthalocyanine by solution in 100% deutero sulfuric acid followed by dilution with deuterium oxide at 0°, and recrystallized from deutero sulfuric acid–deuterium oxide to constant analysis.

Sulfuric acid and deutero sulfuric acid were prepared by cautious addition of the stoichiometric amount of water, or deuterium oxide, to sulfur trioxide. All deuterium oxide used was contaminated with 0.13% protium.

Infrared spectra were run on potassium bromide disks in a Beckman Model IR-7 at resolutions of 2 cm.$^{-1}$ or better.

X-ray analyses indicated that all phthalocyanine preparations were of the *alpha* crystalline modification.[6,7]

Combustion analyses were performed in duplicate on each of two samples to minimize random errors.

H to D ratio was analyzed on a mass spectrometer. The gas used was obtained by reacting the water of combustion with purified sodium.

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[3] A. N. Terenin and A. N. Sidorov, *Spectrochim. Acta Suppl. Int. Cong. Spect.* **9**, 574 (1957).

[4] J. E. Tyler and S. A. Ehrhardt, *Anal. Chem.*, **25**, 390 (1953).

[5] P. A. Barrett, D. A. Frye, and R. P. Linstead, *J. Chem. Soc.*, **1938**, 1157.

[6] G. Susich, *Anal. Chem.*, **22**, 426 (1950).

[7] A. A. Ehret and H. B. Gottlieb, *J. Am. Chem. Soc.*, **74**, 2806 (1952).

Reaction of Malononitrile with Chlorine Near Neutral *p*H

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Received August 31, 1960

Addition of two moles of chlorine to a concentrated aqueous solution of malononitrile at 0° was reported[1] to produce an oily product from which dichloromalononitrile (b.p. 97°/754 mm.) and dichlorocyanoacetamide (m.p. 91°; b.p. 150°/15 mm.) were isolated. It is obvious, although not stated by the authors, that the aqueous malononitrile solution became quite acidic as soon as chlorine introduction was begun and that some dichloromalononitrile separated from the reaction mixture before it could react further with chlorine in the aqueous phase.

The chlorination reported here differs from that cited above in that, in the present investigation, a dilute malononitrile solution was added to hypochlorite at an initial *p*H of 7 and ambient temperature, with continual neutralization of acid formed in the reaction, and in the final molar ratio of chlorine to malononitrile of 2.5. While no attempt was made to isolate volatile products, such as those encountered by Ott and co-workers,[1] or to get a quantitative measure of yield, dichloroacetamide was obtained in about 18% and dichloromalondiamide in about 3% of the theoretical amounts. Carbonate was also detected among the products of reaction. This note concerns itself with explaining the origin of the compounds identified, inasmuch as the rapid hydrolysis of nitrile groups to amide and the replacement of one amide function

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[1] E. Ott and B. Löpmann, *Ber.*, **55**, 1255 (1922), corrected by E. Ott and H. Finken, *Ber.*, **58**, 1703 (1925).

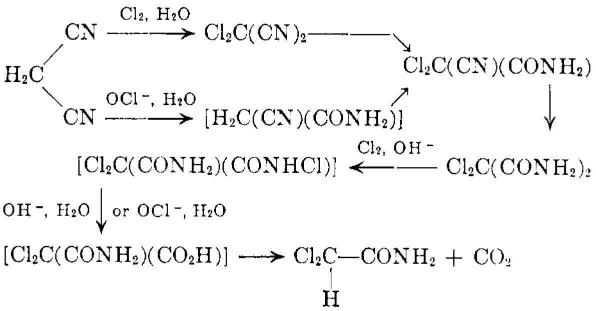
by hydrogen under such mild conditions of pH and temperature may be regarded as unusual. In view of the large proportion of starting material unaccounted for, it should not be construed that the mechanisms discussed here are necessarily the only ones or even the most important ones operative.

From the work of Pearson and co-workers[2] it is evident that the rate of substitution of chlorine for the first hydrogen is dependent upon the rate of proton dissociation from malononitrile, and that the second chlorine enters more rapidly than the first, as the ionization rate is controlled by the electron-withdrawing effects of the substituents on the carbon concerned.[3]

After chlorination has replaced both protons of malononitrile, the next step would appear to be the hypochlorite-catalyzed hydrolysis of nitrile groups. Although the authors can find no instance of this effect in the literature, some close analogies may be drawn, both with respect to the reactant and to the reagent. Thus, hypochlorite ion is a potent catalyst for the hydrolysis of *p*-nitrophenyl acetate[4] and of derivatives of organophosphorus acids.[5] Moreover, perhydroxyl ion, which has a catalytic effect similar to that of hypochlorite ion towards *p*-nitrophenyl acetate[4] and derivatives of organophosphorus acids,[6] is an excellent catalyst for nitrile hydrolysis.[7] Thus, it is quite likely that the observed hydrolysis of the cyano groups is primarily due to the presence of hypochlorite ion.

The authors are unaware of any recorded instance of direct decarboxamidation; it must be conjectured that hydrolysis of one amide group of dichloromalondiamide to carboxyl took place, followed by decarboxylation to dichloroacetamide.[8] Under the mild conditions of the reaction, it seems unlikely that amide hydrolysis should have occurred, except through the effect of the chlorinating agent. A plausible mechanism might involve formation of the *N*-chloroamide followed by hydrolysis, which might or might not be hypochlorite ion-catalyzed. Indeed, hydrolysis of *N*-chloroamides containing strongly electron-withdrawing groups, as an alternative to the Hofmann rearrangement, has been observed.[9] It is improbable that hypochlorite ion should catalyze amide hydrolysis, but perhaps plausible that it should catalyze C—N hydrolysis of the *N*-chloroamide. This would conform with the generalization[10] that, for nucleophilic displacement of a derivative of a carboxylic acid, by a given reagent, the reaction rate increases as the leaving group becomes less basic.

In terms of the products isolated by Ott and co-workers[1] and by ourselves, the degradation of malononitrile with chlorine can now be formulated in an overall scheme involving double C-chlorination of the methylene group, with subsequent (or possibly simultaneous) nitrile hydrolysis, *N*-chlorination of one of the resulting amide groups, hydrolysis of the *N*-chloroamide to carboxyl and decarboxylation to dichloroacetamide, according to the following scheme:



EXPERIMENTAL

Cold chlorine water was adjusted with sodium hydroxide solution to pH 7.05 and titrated to show the presence of 0.0675 mole of chlorine in 612 ml. of water. An aqueous solution containing a total of 0.027 mole of malononitrile was slowly added in two portions: 75 ml. and 20 ml. During the addition of the first portion, 14 ml. of $1N$ sodium hydroxide was added concurrently, with the use of a pH meter, in an effort to keep the pH constant, but the pH rose to 8 by the end of the first addition and then began decreasing very slowly when hydroxide addition was stopped. The second portion of malononitrile was added rapidly without any additional base, with the expectation that the pH would drop; instead, the pH rose suddenly to 9.5, then fell slowly, and the solution turned yellow-brown. Titration indicated the complete loss of active chlorine. After standing overnight, the mixture was taken to dryness on a rotating evaporator and the solid thus obtained was extracted with benzene to give a solution (I) and a residue (II). The benzene solution (I) was evaporated to leave a solid which was recrystallized from

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(2) R. G. Pearson and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953); R. G. Pearson and J. M. Mills, *J. Am. Chem. Soc.*, **72**, 1692 (1950).

(3) This need not imply that the monochloro derivative could not be prepared from a 1:1 ratio of chlorine to malononitrile. Pearson[2] cites an analogous case in which dibromomalonic ester reacts with malonic ester to give bromomalonic ester. In this case, the position of the final equilibrium in the bromination of malonic ester cannot be explained solely on the basis of the reaction rates involved in the initial steps.

(4) W. P. Jencks and Joan Carriuolo, *J. Am. Chem. Soc.*, **82**, 1778 (1960).

(5) J. Epstein, V. E. Bauer, M. Saxe, and M. M. Demek, *J. Am. Chem. Soc.*, **78**, 4068 (1956); A. L. Green, G. L. Sainsbury, B. Saville, and M. Stansfield, *J. Chem. Soc.*, 1583 (1958).

(6) J. Epstein, M. M. Demek, and D. H. Rosenblatt, *J. Org. Chem.*, **21**, 796 (1956); L. Larsson, *Acta Chem. Scand.*, **12**, 723 (1958).

(7) K. B. Wiberg, *J. Am. Chem. Soc.*, **75**, 3961 (1953); **77**, 2519 (1955).

(8) M. Conrad and C. Brückner, *Ber.*, **24**, 2994 (1891), reported the reaction of diethyl dichloromalonate with alcoholic ammonia to give both dichloromalondiamide and dichloroacetamide. It is difficult to account for the latter compound unless water, present in the solvent medium, gave rise to the carboxyl-containing intermediate which thereafter lost carbon dioxide.

(9) C. R. Hauser and W. B. Renfrow, Jr., *J. Am. Chem. Soc.*, **59**, 121 (1937).

(10) M. L. Bender, *Chem. Revs.*, **60**, 61 (1960).

ligroin to give dichloroacetamide, m.p. 96–99° (sublimed easily); lit.,[8,11] m.p. 94.5°, 98°, sublimes easily.[11]

Anal. Calcd. for $C_2H_3ONCl_2$: C, 18.8; H, 2.34; 0, 12.5. Found: C, 19.0; H, 2.4; 0, 12.6.

The residue (II) from benzene extraction was extracted with acetone, solvent was removed, and the viscous water-soluble mass thus obtained was recrystallized twice from benzene to dichloromalondiamide, m.p. 199.5–202°, lit.,[8] m.p. 202°.

Anal. Calcd. for $C_3H_4O_2N_2Cl_2$: C, 21.07; H, 2.36; 0, 18.7. Found: C, 21.4; H, 2.6; 0, 18.4.

The residue left after acetone extraction of residue (II) was dissolved in water and acidified, whereupon carbon dioxide was evolved and identified by its formation of a precipitate with barium hydroxide.

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(11) A. Geuther, *Jahresbericht über die Fortschritte der Chemie*, **17**, 317 (1864).

Synthesis of 1,3,5,7-Tetracyanoheptane

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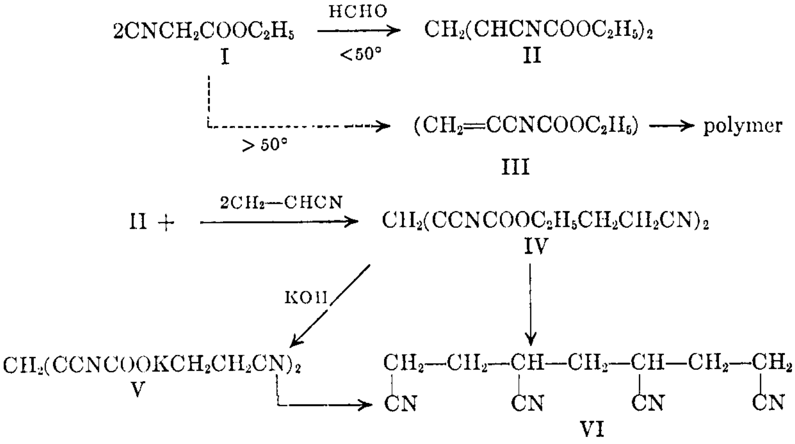
Received September 8, 1960

In a study of the solubility properties of polymers,[1] 1,3,5,7-tetracyanoheptane (VI) was synthesized as a short-chain model for the polyacrylonitrile molecule. VI has the features of a correct nitrile group spacing along a short hydrocarbon chain. The following reaction sequence was used to prepare VI from cyanoacetic ester (I), formaldehyde, and acrylonitrile.



The initial step in the synthesis was the addition of formaldehyde to I. The reaction temperature was very critical and, in numerous instances, only the α-cyanoethylacrylate (III) was formed. III polymerized immediately to a low molecular weight, sticky polymer that plugged the distillation column. Recently, Hellmann and Seegmüller[2] and Brown[3] reported the synthesis of II in which the formation of III was avoided.

EXPERIMENTAL

α,α'-Dicyanodiethylglutarate (II). Paraformaldehyde (60 g., 2 moles) was dissolved in 270 g. (2.39 moles) of cyanoacetic ester (I) and to this solution 4 ml. of 10% potassium hydroxide in ethanol was added during the course of 4 hr. Initially, the reaction was exothermic so it was necessary to cool it to maintain the temperature below 50°. However, in the latter stage of the addition of the potassium hydroxide, heat was required to maintain the desired temperature. After an additional 2 hr. heating and stirring, the reaction mixture was adjusted to a *p*H of 4 with alcoholic hydrochloric acid. It was vacuum-distilled without further treatment. II, 206 g. (73% yield), was collected boiling at 150.5–151.5°/0.4–0.6 mm., n^{24} 1.4500, d_{24} 1.1416.

Anal. Calcd. for $C_{11}H_{14}O_4N_2$: C, 55.46; H, 5.88; 0, 26,80; N, 11.75. Found: C, 55.55, 55.70; H, 5.9, 5.7; O, 26.8, 26.8; N, 11.64, 11.65.

1,3,5,7-Tetracyano-3,5-dicarbethoxyheptane (IV). To a solution of 180 g. (0.756 mole) of II, 300 ml. of dioxane and 102 ml. (1.51 moles) of acrylonitrile was added slowly (1 hr.) 38.5 g. of Triton B while maintaining the temperature between 30–35°. The solution was stirred an additional 16 hr. at this temperature and then poured into 3 l. of distilled water. After acidification to *p*H 4 with acetic acid, the reddish-yellow, oily layer was separated from the aqueous phase and dried by azeotropic distillation with benzene. The crude product (160 g., 60% yield) was not identified but was converted directly to V.

Potassium α,α'-dicyano-α,α'-bis(β-cyanoethyl)glutarate (V). Crude IV (160 g., 0.452 mole) was slowly mixed (0.5 hr.) into a solution of 84 g. of potassium hydroxide dissolved in a mixture of 600 ml. methanol and 400 ml. ethanol. A gummy, reddish-yellow salt precipitated immediately. The supernatent liquid was decanted from the salt and the latter was isolated by repeated washing with cold methanol. A white, free-flowing powder (39 g., 24% yield) was obtained, m.p. 198–206° dec.

Anal. Calcd. for $C_{13}H_8N_4O_4K_2$: C, 43.09; H, 2.21; N, 15.47; K, 21.54. Found: C, 42.9; H, 3.1, 3.4; N, 14.3, 14.4; K, 20.0, 19.8.

The infrared spectrum of V[4] is consistent with the proposed structure.

1,3,5,7-Tetracyanoheptane (VI). V, 30 g. (0.083 mole), was dissolved in 250 ml. of glacial acetic acid and maintained at 90–100° for 2.5 hr. After removal of the acetic acid by vacuum-distillation, the residue was extracted with

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(1) M. K. Phibbs, *J. Phys. Chem.*, 59, 346–53 (1955).

(2) H. Hellmann and K. Seegmüller, *Ber.*, **90**, 535 (1957).

(3) J. C. Brown, this laboratory, private communication.

(4) Dr. R. Zbinden, private communication.